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Patent 2000-386002

[Document Name] Specifications

[Title of the Invention] Porous Polymer Particle, Alkali-Resistant Anion Exchanger, Its Manufacturing Method, Ion Chromatography-Use Column and Anion Measurement Method

[Claims]

[Claim 1] A porous polymer particle that is characterized by a nitrogen containing heterocyclic group, that contains a quaternary ammonium structure, being bonded to an alkali resistant polymer substrate by means of a spacer.

[Claim 2] A porous polymer particle as described in Claim 1 wherein a nitrogen containing heterocyclic group that contains a quaternary ammonium structure is derived from an aromatic or non-aromatic nitrogen containing heterocyclic compound.

[Claim 3] A porous polymer particle as described in Claim 2 wherein the nitrogen containing heterocyclic compound is a compound which can be selected from a group comprised of a pyridine compound that is represented by Formula (1)

[Chemical 1]

(In the formula, R represents an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or halogen atom, or a halogen atom and m is an

integer of 0~5. The plurality of R may be the same or different when m is 2 or more.),

a 1-alkylpyrrolidine compound that can be represented by Formula (2)

[Chemical 2]

(In the formula, R represents an alkyl group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or a halogen group, R<sup>1</sup> represents an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and n is an integer of 0~2.),

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a 1-alkylpiperidine that is represented by Formula (3)

[Chemical 3]

(In the formula, R represents an alkyl group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or a halogen atom, R<sup>1</sup> represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and p is an integer of 0~2.),

and a 1, 4-dialkylpiperidine compound that is represented by Formula (4)

[Chemical 4]

(In the formula,  $R^2$  and  $R^3$  can be identical or different and, respectively, are hydrogen atoms, or alkyl groups of carbon number 1-5 that are also desirable when substituted by a hydroxyl group or halogen atom. However,  $R^2$  and  $R^3$  do not simultaneously represent hydrogen atoms.)

[Claim 4] A porous polymer particle as described in Claim 3 wherein a nitrogen-containing heterocyclic compound is pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine, 1-(2-hydroxyethyl)piperidine, 1-(hydroxymethyl)piperidine, 1-(2-hydroxyethyl)pyrrolidine, 2-(2-hydroxyethyl)-1-methylpyrrolidine, 3-hydroxy-1-methylpiperidine, 4-hydroxy-1-methylpiperidine, 4-chloro-1-methylpiperidine, 1-(2-chloroethyl)piperidine, 1-(2-chloroethyl)pyrrolidine, 1-methylpiperidine, 1-ethylpiperidine or 1, 4-dimethylpiperidine.

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[Claim 5] A porous polymer particle as described in any of Claims 1 through 4 wherein the aforementioned porous polymer particle substrate is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers, the spacer molecule that connects the substrate and ion exchange group is a compound which contains a glycidyl group, and the aforementioned polymer is bonded with the spacer by means of a bond that does not

cleave under alkali conditions.

[Claim 6] A porous polymer particle as described in any of Claims 1 through 5 that has an average particle size of 1~30  $\mu\text{m}$ .

[Claim 7] A porous polymer particle as described in any of Claims 1 through 6 that has an average pore size of 50~300 Å.

[Claim 8] An alkali-resistant anion exchanger that is made from a porous polymer particle as described in any of Claims 1 through 7.

[Claim 9] An alkali-resistant anion exchanger manufacturing method that is characterized by a spacer molecule that contains a glycidyl group being bonded to an alkali-resistant polymer porous particle that is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers by means of a bond which does not cleave under alkali conditions, and the introduction of a quaternary ammonium group that is an anion exchange group by reacting a nitrogen containing heterocyclic compound with the aforementioned glycidyl group.

[Claim 10] An alkali-resistant anion exchanger as described in Claim 9 wherein a nitrogen containing heterocyclic compound is selected from the nitrogen containing heterocyclic compounds that are described in Claims 2 or 3.

[Claim 11] An alkali-resistant anionic exchanger manufacturing method as described in Claim 10 that is characterized by a glycidyl group containing group such as the mass becoming 104~135 after the reaction when the mass of the aforementioned poly(vinyl alcohol) type copolymer is 100, by reacting a compound

that contains 2 or more glycidyl groups in the molecule with a poly(vinyl alcohol) type copolymer with a hydroxyl group by saponifying one part of a vinyl carboxylate and isocyanurate type cross-linking monomer copolymer as a hydroxyl group.

[Claim 12]        An        alkali-resistant        anion        exchanger  
manufacturing method

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as described in Claim 11 with saponification of a poly(vinyl alcohol) type polymer performed until 0.5~5 meq/g of hydroxyl group is produced in the polymer.

[Claim 13]        A suppressor system ion chromatography column-use packing that is made from an anion exchanger as described in Claim 8.

[Claim 14]        A suppressor system ion chromatography-use column that is packed with anion exchanger as described in Claim 8.

[Claim 15]        An anion measurement method by suppressor system ion chromatography with a column as described in Claim 14 and an alkali eluent used in combination.

[Claim 16]        An anion measurement method as described in claim 15 wherein an alkali eluent is a hydroxide type eluent.

[Claim 17]        An anion measurement method as described in Claim 16 that uses a hydroxide type eluent at an isocratic condition of 20 mM or less as an alkali eluent.

[Detailed Explanation of the Invention]

[0001]

[Technical Field to Which the Invention Belongs]

This invention pertains to an alkali-resistant anion exchanger and a suppressor system ion chromatography-use column that uses the anion exchanger. Also, when concretely stated, [this invention] pertains to a suppressor system ion chromatography-use alkali-resistant anion exchanger that can analyze inorganic anions like fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, sulfate ions, and phosphate ions with good separation in a short time period in isocratic (*isocratic*) conditions using a constant concentration of hydroxide type eluent, its manufacturing method, a suppressor system ion chromatography-use column that uses that anion exchanger, and an anion measurement method that uses that column.

[0002]

[Background Art]

The analysis of 7 kinds of ions is important in analysis by water testing or the analysis of food: fluoride ions ( $F^-$ ), chloride ions ( $Cl^-$ ), nitrite ions ( $NO_2^-$ ), bromide ions ( $Br^-$ ), nitrate ions ( $NO_3^-$ ), sulfate ions ( $SO_4^{2-}$ ), phosphate ions ( $PO_4^{3-}$ ).

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These ions are called "7 Kinds of Standard Inorganic Anions". Currently, ion chromatography is utilized as an effective and highly accurate, highly sensitive means for analysis of inorganic anions that contain these 7 kinds of standard inorganic anions.

[0003]

In ion chromatography, a sample which contains an ion species is injected into the column while an eluent is fed into the ion

exchange column, the ions (kind, amount) that are separated out by the column by having differences in [their] retention times are detected by a high sensitivity detector like an electrical conductivity detector; this chromatography is a "suppressor system" that uses a suppressor or a "non-suppressor system" that does not use a suppressor. The suppressor is a device with a cation in the liquid displaced by a hydrogen ion, as shown in Figure 1, that is connected between the separation column and detector, and has the role of decreasing the background when an ion is detected by an electrical conductivity detector and thus increasing the measurement sensitivity.

[0004]

Therefore, things like a mixed solution of sodium carbonate and sodium hydrogen carbonate, a boric acid buffer, an aqueous sodium hydroxide solution or an aqueous potassium hydroxide solution are passed through as the eluent in a "suppressor system" and ions are detected by a conductivity detector by means of a suppressor after the sample ions are separated by the separation column. The electrical conductivity that is measured by the detector is recognized as a signal superposed with the contribution from the ion species in the sample with the electrical conductivity of the eluent itself as the background, and the suppressor improves the measurement sensitivity of the signal for ion species in a sample by decreasing the background electrical conductivity by converting things like a salt or base in the eluent to things like an acid with a lower degree of dissociation.

A suppressor system requires an exclusive device as compared with a non-suppressor system and is economically worse, but this method is indispensable for the regulation of things like pure water and chemicals that are used in [fields] like the semiconductor field.

[0005] The ideal in anion analysis by ion chromatography is balancing good separation with a limited short analysis time insofar as possible for the 7 kinds of standard inorganic anions. However, fluoride ions are difficult to retain on an anion exchanger in a separation column

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and quickly passes through the column. The result is that the separation of the signal peak due to the fluoride ion and the water dip (a negative peak that is generated by the eluent being diluted due to the injection of a sample) becomes inadequate and the determination precision easily deteriorates.

The use of eluents with weak elution strength can be considered for improving the retention of fluoride ions, but, in this case, a lengthening of the analysis time occurs due to extreme lengthening of the elution time of divalent or higher valence anions (sulfate ions and phosphate ions). In particular, this problems is extreme when the eluent is alkaline. Thus, the process must be in analysis conditions for simultaneous analysis of fluoride ions and divalent or higher valence anions.

[0006]

Therefore, a method that overcomes the above-mentioned



problems by optimizing the eluent composition was investigated. For example, a method was disclosed wherein boric acid is added to a weakly acidic mobile phase in a non-suppressor system and anionic compounds are generated by selective reaction of this boric acid with fluoride ions, and the retention is improved (Publication of Japanese Examined Patent No. H7-37972). Further, the improvement of fluoride ion retention by varying the respective composition ratios when a mixed solution of sodium carbonate and sodium hydrogencarbonate is used as the eluent in a suppressor system is known. Also, a method with a salt of boric acid added to the eluent in a suppressor system was also disclosed (Publication of Japanese Laid-Open Patent No. 2000-180429). When the eluent can be composed of a plurality of components like this, there are corresponding possibilities by varying the composition.

[0007]

However, hydroxide type eluents like aqueous sodium hydroxide solution and aqueous potassium hydroxide solution, which are used as eluents of suppressor systems, cannot overcome the problems for elution because, usually, a single component is utilized; thus, a specific means must be used for measurement for realizing both the improvement of the retention of fluoride ions and the shortening of the elution time of divalent or higher valency anions (in particular, phosphate among the 7 kinds of standard inorganic anions) in suppressor systems that use alkaline eluents like this.

Method performed in prior [art] are of 2 groups, one is a gradient analysis method that uses concentration gradient for the

eluent and the other one is a method that uses a high concentration eluent of approximately 40 mM by establishing a large ion exchange capacity of the ion exchanger that is packed in the column.

[0008]

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However, the first method has problems like requiring the application of at least 2 types of solutions that have different concentrations for imparting a concentration gradient, and equipment and operations that absorb and mix these by using 2 pumps; also, there is the requirement of a stabilizing time until the eluent concentration returns to the origin[al concentration] for each measurement. Further, the second method has problems such as shortening the suppressor life by requiring high voltage for the electrodialysis by a suppressor device that uses a continuous regeneration type of ion exchange membrane, which is currently widely utilized, due to the eluent concentration being high.

[0009]

Further, not only the realization of both improving the retention of the above-mentioned fluoride ion and the shortening of the elution time of the phosphate ion when analyzing tap water by a suppressor system that uses a hydroxide type eluent, but simultaneous adequate separation of the chloride ions and nitrite ions must also be realized. This is because analysis of nitrite ions to an extent of a number of ppb in the presence of a number of tens of ppm of chloride ions is necessary in tap water analysis. The simultaneous realization of the analysis of a trace amount of

nitrite ions was complex because the separation of chloride ions and nitrite ions was inadequate since, even if adequate, carbonate ions elute between [those] by prior [art] columns that are used with hydroxide type eluents.

[0010]

The applicant previously proposed a manufacturing method for an anion carrier that is obtained by introducing a tertiary heterocyclic amine into an acrylate or methacrylate type polymer by means of a spacer and a column that was packed with this (Publication of Japanese Laid-Open Patent No. 2000-221179). However, this is as a non-suppressor type ion chromatography-use column that uses an acidic eluent and a method that manufactures the packing material, and is not one that measures anions with a suppressor type ion chromatography-use column that uses an alkaline eluent.

[0011]

[Problems to be Solved by the Invention]

This invention, in view of such circumstances, has the objective of offering an ion exchanger of ion chromatography-use that can suppress the elution time of the phosphate ions to a short time of ten minutes~a number of tens of minutes without being done by gradient analysis (that is, under isocratic conditions of a constant concentration) by using a low concentration (for example, 20 mM or less) eluent in a suppressor system ion chromatography that uses a hydroxide type eluent,

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adequately separate fluoride ions, which are difficult to retain, from the water dip, and adequately separate the chloride ions and nitrite ions, its manufacturing method, a suppressor system ion chromatography column-use packing that uses this anion exchanger, an ion chromatography-use column and a precise anion measurement method at low cost that uses this column.

[0012]

[Means for Solving the Problems]

These inventors attained the realization of this invention by discovering that the 7 kinds of standard inorganic anions can be well separated by using a column that is packed with alkali-resistant high strength anion exchanger which is made from a porous polymer which uses a structure with a nitrogen containing heterocyclic group that contains a quaternary ammonium or pyridinium bonded to an alkali-resistant polymer substrate by means of a spacer as the result of diligent research that should solve the above-mentioned problems.

[0013]

That is, this invention pertains to porous polymer particles, alkali resistant anion exchanger, its manufacturing method, a suppressor system ion chromatography column-use packing that is made from this anion exchanger, a suppressor system ion chromatography-use column and an anion measurement method that uses this column.

[0014]

1. A porous polymer particle that is characterized by a nitrogen

containing heterocyclic group, that contains a quaternary ammonium structure, being bonded to an alkali resistant polymer substrate by means of a spacer.

2. A porous polymer particle as described in the above-mentioned 1 wherein a nitrogen containing heterocyclic group that contains a quaternary ammonium structure is derived from an aromatic or non-aromatic nitrogen containing heterocyclic compound.

[0015]

3. A porous polymer particle as described in the above-mentioned 2 wherein the nitrogen containing heterocyclic compound is a compound which can be selected from a group comprised of a pyridine compound that is represented by Formula (1)

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[Chemical 5]

(In the formula, R represents an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or halogen atom, or a halogen atom and m is an integer of 0~5. The plurality of R may be the same or different when m is 2 or more.),

a 1-alkylpyrrolidine compound that can be represented by Formula (2)

[Chemical 6]

(In the formula, R represents an alkyl group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or a halogen group, R<sup>1</sup> represents an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and n is an integer of 0~2.),

a 1-alkylpiperidine that is represented by Formula (3)

[Chemical 7]

(In the formula, R represents an alkyl group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or a halogen atom, R<sup>1</sup> represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and p is an integer of 0~2.),

and a 1, 4-dialkylpiperidine compound that is represented by Formula (4)

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[Chemical 8]

(In the formula, R<sup>2</sup> and R<sup>3</sup> can be identical or different and, respectively, are hydrogen atoms, or alkyl groups of carbon number 1~5 that are also desirable when substituted with a hydroxyl group or halogen atom. However, R<sup>2</sup> and R<sup>3</sup> do not simultaneously represent a hydrogen atom.)

[0016]

4. A porous polymer particle as described in the above-mentioned 3 wherein a nitrogen-containing heterocyclic compound is pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine, 1-(2-hydroxyethyl)piperidine, 1-(hydroxymethyl)piperidine, 1-(2-hydroxyethyl)pyrrolidine, 2-(2-hydroxyethyl)-1-methylpyrrolidine, 3-hydroxy-1-methylpiperidine, 4-hydroxy-1-methylpiperidine, 4-chloro-1-methylpiperidine, 1-(2-chloroethyl)piperidine, 1-(2-chloroethyl)pyrrolidine, 1-methylpiperidine, 1-ethylpiperidine or 1, 4-dimethylpiperidine.

[0017]

5. A porous polymer particle as described in any of the above-mentioned 1 through 4 wherein the aforementioned porous polymer particle substrate is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers, the spacer molecule that connects the substrate and ion exchange group is a compound which contains a glycidyl group, and the aforementioned polymer is bonded with the spacer by means of a bond that does not cleave under alkali conditions.

6. A porous polymer particle as described in any of the above-mentioned 1 through 5 that has an average particle size of 1-30  $\mu\text{m}$ .

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7. A porous polymer particle as described in any of the above-mentioned 1 through 6 that has an average pore size of 50-300 Å.

[0018]

8. An alkali resistant anion exchanger that is made from a porous polymer particle as described in any of the above-mentioned 1 through 7.

9. An alkali resistant anion exchanger manufacturing method that is characterized by a spacer molecule that contains a glycidyl group being bonded to an alkali-resistant polymer porous particle that is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers by means of a bond which does not cleave under alkali conditions, and the introduction of a quaternary ammonium group that is an anion exchange group by reacting a nitrogen containing heterocyclic compound with the aforementioned glycidyl group.

10. An alkali-resistant anion exchanger as described in the above-mentioned 9 wherein a nitrogen containing heterocyclic compound is selected from the nitrogen containing heterocyclic compounds that are described in the above-mentioned 2 or 3.

[0019]

11. An alkali-resistant anionic exchanger manufacturing method as described in the above-mentioned 10 that is characterized by a glycidyl group containing group such as the mass becoming 104-135 after the reaction when the mass of the aforementioned poly(vinyl alcohol) type copolymer is 100, by reacting a compound that contains 2 or more glycidyl groups in the molecule with a poly(vinyl alcohol) type copolymer with a hydroxyl group by saponifying one part of a vinyl carbonate and isocyanurate type



cross-linking monomer copolymer as a hydroxyl group.

12. An alkali-resistant anion exchanger manufacturing method as described in the above-mentioned 11 with saponification of a poly(vinyl alcohol) type polymer performed until 0.5~5 meq/g of hydroxyl group is produced in the polymer.

13. A suppressor system ion chromatography column-use packing that is made from an anion exchanger as described in the above-mentioned 8.

[0020]

14. A suppressor system ion chromatography-use column that is packed with anion exchanger as described in the above-mentioned 8.

15. An anion measurement method by suppressor system ion chromatography with a column as described in the above-mentioned 14 and an alkali eluent used in combination.

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16. An anion measurement method as described in the above-mentioned 15 wherein an alkali eluent is a hydroxide type eluent.

17. An anion measurement method as described in the above-mentioned 16 that uses a hydroxide type eluent at an isocratic condition of 20 mM or less as an alkali eluent.

[0021]

[Actual Embodiment of the Invention]

This invention is explained in detail, below.

(A) Nitrogen Containing Heterocyclic Compound

An aromatic or non-aromatic nitrogen containing heterocyclic compound is used as the raw material of the nitrogen containing

heterocyclic group which has a quaternary ammonium structure. These compounds are also desirable as having a substituent on the ring forming carbon atoms insofar as an obtained anion exchanger can function.

The (substituted) pyridine compounds that are represented by the following Formula (1) can be included as aromatic nitrogen containing heterocyclic compounds.

[Chemical 9]

In the formula, R represents an alkyl group or alkoxy group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or a halogen atom, or a halogen atom, and m is an integer of 0-5. When m is greater than 2, the plurality of R may be identical or different.

Further, 1-(substituted) alkylpyrrolidine compounds that are represented by the following Formula (2), 1-(substituted) alkylpiperidine [compounds] which are represented by Formula (3) and 1-4-di(substituted) alkylpiperidine compounds that are represented by Formula 4 can be included as non-aromatic nitrogen containing heterocyclic compounds.

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[Chemical 10]

In Formula (2), R represents an alkyl group of carbon number 1~5 which is also desirable when substituted by a hydroxyl group or a halogen atom, R<sup>1</sup> represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and n is an integer of 0~2.

In Formula (3), R represents an alkyl group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or a halogen atom, R<sup>1</sup> represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and p is an integer of 0~2.

In Formula (4), R<sup>2</sup> and R<sup>3</sup> are desirable as being identical or different and are respectively alkyl group of carbon numbers of 1~5 that are also desirable when substituted by a hydroxyl group or a halogen atom. Further, R<sup>2</sup> and R<sup>3</sup> do not simultaneously represent a hydrogen atom.

[0022]

Concrete examples of aromatic nitrogen containing heterocyclic compounds includes ones like pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxypyridine, 3-hydroxypyridine and 4-hydroxypyridine.

[0023]

Concrete examples of non-aromatic nitrogen containing heterocyclic compounds include ones like 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine, 1-(2-hydroxyethyl)piperidine, 1-(hydroxymethyl)piperidine, 1-(2-

hydroxyethyl)piperidine, 2-(2-hydroxyethyl)-1-methylpyrrolidine, 3-hydroxy-1-methylpiperidine, 4-hydroxy-1-methylpiperidine, 4-chloro-1-methylpiperidine, 1-(2-chloroethyl)piperidine,

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1-(2-chloroethyl)pyrrolidine, 1-methylpiperidine, 1-ethylpiperidine and 1,4-dimethylpiperidine.

[0024]

(B) Anion Exchanger and Its Manufacturing Method

Ones like alkali-resistant porous chemical bond type ion exchangers and pellicular type ion exchangers can be included as embodiments of the packing material that is manufactured by introducing the above-mentioned ion exchange group.

[0025]

(1) Porous Chemical Bond Type Ion Exchangers

Porous chemical bond type ion exchangers that can be suitably used in this invention are ones with ion exchange groups by bonding the above-mentioned nitrogen containing heterocyclic compounds to an alkali-resistant polymer by means of a spacer.

[0026]

The porous polymers that can be used as the porous chemical bond type ion exchanger substrate are not particularly limited when [they are] alkali-resistant. Ones like poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers can be included as examples of this kind of polymer.

The spacer molecule, which has a group that is capable of bonding with a tertiary heterocyclic amine compound, is bonded to

these alkali-resistant porous polymers and an ion exchange group is produced by then reacting a tertiary heterocyclic amine compound with this.

[0027]

The spacer molecule provides a plurality of atoms between the substrate surface and ion exchange group, usually more than 3 atoms and less than 20, and is bonded with the alkali-resistant porous polymer at one end and with the ion exchange group at the other end. The result is that [the molecule] acts as a spacer which lengthens the distance between both parties and has the function of controlling peak diffusion by suppressing ion-substrate interference.

Compounds that contain a glycidyl group which bonds with tertiary heterocyclic amine compounds are desirable as spacer molecules. Ones like epichlorohydrin, 1,4-butanediol diglycidyl ether, ethylene glycol diglycidyl ether and glycerol glycidyl ether can be included as concrete examples.

[0028]

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## (2) Porous Chemical Bond Type Ion Exchanger Manufacturing Method

The bond of the spacer molecule with the alkali-resistant porous polymer is desirable when cleaving does not occur at pH conditions used in anion analysis.

The manufacturing method is not particularly limited, but manufacturing can be by methods where an ester bond is contained in an alkali resistant porous polymer and reacts with a diglycidyl

compound which contains 2 or more glycidyl groups in the same molecule as the spacer molecule with a hydroxyl group by saponifying this [polymer], for example. The schematic below shows one example of a 1-methylpiperidine introduced to a hydroxyl group of a substrate by means of 1,4-butanediol diglycidyl ether as a spacer.

[0029]

[Chemical 11]

[0030]

When [this method] is concretely explained in detail by taking an alkali-resistant poly(vinyl alcohol) type copolymer as an example, one part of the ester group of the copolymer is converted to a hydroxyl group by saponifying of the copolymer with a vinyl carboxylate and a cross-linkable monomer that has an isocyanurate ring. The hydrophilicity of the substrate is increased and the interference with the ion is controlled by this, and the hydroxyl group becomes an active site necessary for reacting with the spacer molecule. A compound that contains 2 or more glycidyl groups within the same molecule, like 1,4-butanediol diglycidyl ether, is reacted with this.

[0031]

The saponification is desired to be such that the hydroxyl group is present at least 0.5 meq/g or more, but 5 meq/g or less,

desirably 1.0~3 meq/g, for adequate introduction of the glycidyl group containing group that reacts with a tertiary heterocyclic amine. Introduction of the required glycidyl group containing group becomes difficult when the hydroxyl group is less than 0.5 meq/g, as does improving the performance of the column because the particle size of the substrate decreases by decreasing the strength of the substrate when 5 meq/g is exceeded,

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thus [both cases] are undesirable.

The amount of hydroxyl group is determined by reacting the hydroxyl group with acetic anhydride and determining the amount of anhydrous acetate that is consumed or the change in the weight after the reaction. At this time, determination can be by the above-mentioned methods after the functional group is protected for cases where the functional group of the substrate also reacts. The amount of hydroxyl group, when 1 g of dried substrate is reacted with 1 mmol of acetic anhydride, is 1 mmol/g.

[0032]

Further, the vinyl carboxylate that is preferably used in this method is a compound that has one or more polymerizable vinyl carboxylate groups and ones like, for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate and vinyl pivalate can be included. These can be used independently or by combining two or more types. Among these, vinyl acetate and vinyl propionate, which are hydrophilic and facilitate polymerization and saponification, are preferably used.

[0033]

As a preferred example of an isocyanurate type cross-linking monomer, cross-linking monomers that have isocyanurate rings which are represented by the following general formula can be included:

[Chemical 12]

[0034]

(In the formula,  $R^4$ ,  $R^5$  and  $R^6$ , respectively and independently, represent  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ,  $-\text{CH}_2-\text{C}\equiv\text{CH}$  or  $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ ). In this, triallyl cyanurate with  $R^4$ ,  $R^5$  and  $R^6$  all being  $-\text{CH}_2\text{CH}=\text{CH}_2$  is preferred as a cross-linking agent with good copolymerizability with vinyl acetate and high stability even for saponification.

[0035]

The mass increase after the glycidyl compound reaction, when the mass of the poly(vinyl alcohol) type copolymer

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is 100, is 104~135. The mass increase is not desired to be less than 104 because the alkali resistance is becomes inadequate, but exceeding 135 is undesirable because the particles become soft and the association of the particles themselves occurs. The mass increase after the glycidyl compound reaction is desired to be 108~130, more desirably 112~125.

[0036]



The anion exchanger that is obtained by the above-mentioned method is a porous particle. The pore size of the porous particle is 50~300 Å, desirably 50~150 Å and more desirably 50~100 Å. The pore size being less than 50 Å is not desirable because the introduction of the glycidyl group containing group to inside the pores becomes difficult. Exceeding 300 Å is not desirable because the strength of the particles is decreased. Methods that are generally performed for high-performance liquid chromatography packing materials are used for controlling the particle size.

The pore size can be determined by ones like reverse size exclusion chromatography that is described by *J.Chromedogr.*, 387(1987) 65, or by a BET (*Brunauer-Emmett-Teller*) method; however, unless otherwise specifically indicated, the average pore size was determined according to the method as described in *Angw. chem. Int. Ed. Engl.*, 17. 901~908(1978).

First, for measurement, the particles to be measured are packed in a column, [this column] is connected to an HPLC apparatus, THF is used as the eluent, and the retention capacity of a plurality of standard polystyrenes and benzenes that cover a wide range of molecular weights are respectively measured. The results are plotted on a graph where with the molecular weight  $M$  (easily seen on a logarithmic scale) is graduated on the Y-axis and the retention capacity (mL) is graduated on the X-axis. A curve with the thus obtained respective points smoothly connected is called a calibration curve. The exclusion limit points ( $V_1$ ,  $M_1$ ) are determined by ordinary methods from the calibration curve and the

straight line  $X=(V_1+V_2)/2$  is drawn on the graph using the measuring point ( $V_2$ , 78) of benzene with this. The average pore size  $\phi_m[\text{\AA}]$  is calculated by substituting the following Formula (X) in the same way with the empirical formula (11) of the above-mentioned cited reference p. 905 by reading the Y coordinate  $M_m$  of the node (called the average pore point) of the straight line and calibration curve.

[Equation 1]

$$\phi_m[\text{\AA}] = 0.62x(M_m)^{0.59} \quad (X)$$

Further, the "average pore point" is defined by the present inventors. [This] means that the point where the integrated volume from the minimum volume (a size where benzene just fits) becomes 50% when the entire pore volume is 100%.

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The above equation is used for converting the standard polystyrene equivalent molecular weight of this point to the pore diameter that just fits.

[0037]

### (3) Pellicular Type Ion Exchanger

A pellicular type ion exchanger is a particle that is made by coating a core particle surface with latex with an ion exchange group introduced. The core particle can include [ones like] sulfonated polystyrene.

[0038]

The particle size of an anion exchanger of this invention is desirable as 1~30  $\mu\text{m}$ , more desirably 2~20  $\mu\text{m}$  and, even more

desirably, is 2~10  $\mu\text{m}$  for a porous chemical bond type. The particle size of a resin for a pellicular type is ordinarily to an extent of 5~15  $\mu\text{m}$ . The decrease of the theoretical plates of a column is undesirable when the particle size of the anion exchanger exceeds 30  $\mu\text{m}$ , while the increase of column pressure becomes large and the packing is extremely difficult when the particle size is less than 1  $\mu\text{m}$ .

The particle size for this invention is a value that is measured by a Coulter counter (*Coulter Counter*).

[0039]

(C) Ion Chromatography Use Column

The packing of the anion exchanger of this invention into an ion chromatography-use column is performed according to conventional packing methods like the slurry method. A column pertaining to this invention is used as a high sensitivity suppressor system ion chromatography-use column having alkali-resistant properties.

[0040] A column that uses an anion exchanger by this invention is stable for eluents (ones like a mixed solution of sodium carbonate and sodium hydrogencarbonate, phosphate buffers, aqueous sodium hydroxide solutions and aqueous potassium hydroxide solutions) that are used in suppressor system ion chromatography, in particular, [ones] useful for use by combining with a pH9~12 alkaline eluent, and for use by combining with a hydroxide type eluent that contains a hydroxide ion as the anion.

[0041]

(D) Anion Measurement Method

An anion measurement method that uses a suppressor system ion chromatography-use column of this invention can be performed according to prior [art] suppressor system ion chromatography.

The total measurement cost can be decreased due to not requiring things like specific measurement devices and concentration preparations and not requiring the application of high voltage for suppressors due to being under isocratic conditions of a set concentration and being able to utilize a low concentration eluent of 20 mM or less even when using a hydroxide type eluent which previously could not be obtained without using a gradient method or high concentration solutions.

[0042]

In this way, the main anions (phosphate ions, fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, and sulfate ions) can be well separated by the suitable selection of eluent concentration even by using a hydroxide type eluent, not only in the case of carbonic acid type eluent and boric acid type eluent, by utilizing suppressor system ion chromatography-use columns that use an anion exchanger of this invention.

[0043]

Thus, [this] is useful for things like trace component analysis in the environment, such as anions in air, water (like river water, tap water, spa water, limnetic water, and drainage), and soil extract solution; analysis of things like food and

fertilizer; anion analysis of things like cosmetic raw materials; anion analysis of coating raw materials, coating materials and surface treatment solutions; analysis of ultrapure water, mixed acids, air, lead frames and wafers in the semiconductor field; quality control in the pharmaceutical field; and the analysis of things like circulating water and cooling water at electric power plants.

[0044]

[Examples]

This invention is explained in further detail by the Examples and Comparative Examples below. However, these are simple representations and the invention is by no means limited to these examples.

[0045]

Example 1:

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A poly(vinyl alcohol) type compound that is prepared by the following method was used as the substrate resin with an ion exchanger introduced. A uniformly mixed solution of 100 g of vinyl acetate, 180 g of 2,2-triallyl isocyanurate, 150 g of butyl acetate and 10 g of azobisisobutyronitrile and 1400 mL of water with a small amount of poly(vinyl alcohol) and sodium phosphate dissolved were charged into a 5 L three-necked flask equipped with a reflux condenser and stirred for 10 minutes. Then, a particulate polymer was obtained by performing polymerization for 16 hours at 60°C while stirring under a nitrogen stream. The polymer was filtered,

washed and extracted with acetone, then dried.

[0046]

The obtained polymer and 3 L of aqueous 1 N sodium hydroxide (NaOH) solution were charged into a 5 L three-necked flask equipped with a reflux condenser, a nitrogen inlet tube and a stirrer; saponification of the polymer was performed by stirring for 20 hours at 15°C under a nitrogen stream, then filtering, washing and drying. The density of the hydroxyl group of the poly(vinyl alcohol) polymer that was obtained by saponification was 2.1 meq/g. An ion exchanger was manufactured by the following procedure with this as a substrate.

[0047]

100 g of the above-mentioned dried polymer, 300 g of 1,4-butanediol diglycidyl ether (referred to as "1,4-BGE" below), 300 mL of dimethylsulfoxide and 65 mL of 30 weight% aqueous sodium hydroxide solution were charged into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a glycidyl group containing group was introduced to the polymer substrate by stirring for 12 hours at 35°C in a nitrogen stream. After the introduction, the polymer was washed with dimethyl sulfoxide and water, then dried by a vacuum dryer. After drying, the weight of the polymer was 110 g, an increase of 10% more than the original substrate.

[0048]

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 4 g of 1-

methylnpiperidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a tertiary heterocyclic amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and, after being treated for 5 hours at 60°C, was washed and dried. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and

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an ion exchange capacity of 20  $\mu\text{eq/g}$ .

[0049]

An anion exchange column was prepared by packing this anion exchanger into a 4.0 mm internal diameter, 250 mm long polyether ethyl ketone resin (PEEK)-made column. Using a DX-320 [manufactured by Dionex Corporation (*Dionex Corporation*)] equipped with a suppressor as an ion chromatograph, 25  $\mu\text{L}$  of an aqueous solution containing 2 mg/L of  $\text{F}^-$ , 3 mg/L of  $\text{Cl}^-$ , 5 mg/L of  $\text{NO}_2^-$ , 10 mg/L of  $\text{Br}^-$ , 10 mg/L of  $\text{NO}_3^-$ , 15 mg/L of  $\text{SO}_4^{2-}$  and 15 mg/L of  $\text{PO}_4^{3-}$  was injected in an ion chromatograph as the standard with 15 mM of aqueous sodium hydroxide solution as the eluent flowing at 1.0 mL/min with a column temperature of 35°C. The obtained chromatograph is shown in Figure 2.

[0050]

Example 2:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate

resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 1 g of 1-methylpyrrolidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing a tertiary heterocyclic amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C. The anion exchanger which was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0051]

Example 3:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 10 g of pyridine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and



introducing a tertiary heterocyclic amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0052]

Comparative Example 1:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 75 mL of a 1% aqueous trimethylamine solution and 500 ml of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing an aliphatic tertiary amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and was washed and dried after treated

for 5 hours at 60°C. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0053]

Comparative Example 2:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was prepared by charging 100 g of glycidyl group containing group introduced polymer, 150 mL of an aqueous 1% triethylamine solution and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing an aliphatic tertiary amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C.

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The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same

column as in Example 1 and measured in the same manner as in Example 1.

[0054]

Example 4:

A styrene/divinylbenzene type [resin] prepared by the following method was used as a substrate resin into which an ion exchange group was introduced. A uniform mixed solution made from 105 g of 4-acetoxystyrene, 70 g of m-divinylbenzene, 75 g of toluene and 3.5 g of 2,2-azobisisobutyronitrile were suspended in 1250 mL of water with 10% poly(vinyl alcohol) dissolved and homogenized. Then, [this] was transferred to a 2 L separable flask and a particulate polymer was obtained by performing polymerization for 6 hours at 70°C. The polymer was filtered and washed with water and acetone and 3-6  $\mu\text{m}$  particles were obtained by classification by air separation after air drying. 150 g of the above-mentioned dried polymer was suspended in 1500 mL of methanol and a solution with 150 g of KOH dissolved in 1500 mL of an aqueous 50% methanol solution was added, and [this] was saponified by stirring for 6 hours at 50°C. 135 g of polymer was recovered after washing this with water and acetone, then drying.

[0055]

100 g of the aforementioned dried polymer, 400 g of 1,4-BGE, 300 mL of dimethyl sulfoxide and 65 mL of water were charged into a 2 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and a glycidyl group containing group was introduced to the polymer substrate by stirring for 16 hours at 35°C under a nitrogen

stream. After introduction, the polymer was washed with dimethyl sulfoxide and water, then dried with a vacuum dryer. After drying, the mass of the polymer was 105 g and increased 5% more than the original substrate.

[0056]

An anion exchanger was prepared by charging 100 g of glycidyl group containing group introduced polymer, 8 g of 1-methylpiperidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a tertiary heterocyclic amine by stirring for 4 hours at 40°C. An ion exchanger was obtained by washing according to the same formulation as Example 1.

The anion exchanger obtained above was packed into the same column as in Example 1

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and measured in the same manner as in Example 1.

[0057]

Comparative Example 3:

The measurement was performed in the same manner as in Example 1 using a column (pellicular type ion exchanger with a tertiary alkanolamine introduced) that is currently commercially available for hydroxide type eluent use.

[0058]

Evaluation:

The kind of tertiary amine introduced, the difference in the retention time between the fluoride ion and the water dip, the

separation degree of the chloride ion and nitrite ion and the retention time of the phosphate ion are shown in Table 1 for Examples 1~4 and Comparative Examples 1~3. The difference in the retention time between fluoride ion and water dip was determined by using the respective peaks as the retention times. The separation degree R of chloride ion and nitrite ion was determined by the following formula.

[0059]

[Equation 2]

$$R=2X(t_2-t_1)/(w_1+w_2)$$

Here,  $t_1$  and  $t_2$  represent the respective retention times and  $w_1$  and  $w_2$  represent respective peak widths.

[0060]

[Table 1]

		④ 導入した三級アミン	⑤ フッ化物イオンと ウォーターデップの 保持時間差(分)	⑥ 塩化物イオンと 亜硝酸イオンの 分離度(R)	⑦ リン酸イオンの 保持時間 (分)
①	実施例 1	1-ナフチルペリジン ⑧	1.00	5.2	15.6
	実施例 2	1-ナフチルピリジン ⑨	0.95	5.0	15.2
	実施例 3	ピリジン ⑩	0.90	5.0	15.8
	実施例 4	1-ナフチルペリジン ⑪	0.85	5.5	19.6
②	比較例 1 (市販品)	TMAH アミン ⑫	ピークが重なって いるため測定不能	⑬ 1.8	34.0
③	比較例 2	トリメチルアミン ⑭	0.79	3.4	16.0
	比較例 3	トリエチルアミン ⑮	0.68	3.2	14.1

[Key to Table 1]

- 1 Example 1, 2, etc.
- 2 Comparative Example 1  
(Commercial Product)
- 3 Comparative Example 2, etc.
- 4 Introduced Tertiary Amine  
Difference in Retention Time of Fluoride Ion and Water  
Dip (Minutes)
- 6 Separation Degree of Chloride Ion and Nitrite Ion (R)
- 7 Retention Time of Phosphate Ion (Minutes)
- 8 1-methylpiperidine
- 9 1-methylpyrrolidine
- 10 pyridine
- 11 1-methylpiperidine
- 12 alkanolamine
- 13 trimethylamine
- 14 triethylamine
- 15 immeasurable due to overlapping of peaks

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[0061]

The retention time of the phosphate ion is extremely long and 30 minutes or more, the fluoride ion is partially overlapped by the water dip and the separation of the chloride ion and sulfite ion is inadequate by the column, which is currently commercially available, that is shown in Comparative Example 1. However, the suppressor system ion chromatograph-use column that uses the anion

exchanger which is prepared by introducing a tertiary heterocyclic amine of this invention, which is shown in Examples 1, 2 and 3, can adequately separate fluoride ions from the water dip and can also adequately separate chloride ions and nitrite ions even when the retention time of the phosphate ion, which is difficult to elute, is set to 14 to 16 minutes. This shows significant improvement as compared with anion exchangers of Comparative examples 2 and 3 with acyclic tertiary amine introduced. Further, the substrate resin not being limited to poly(vinyl alcohol) type resins but the introduction of a heterocyclic amine also being effective for other resins is revealed from Example 4.

[0062]

[Effects of the Invention]

A suppressor system ion chromatograph-use column that is packed with an anion exchanger of this invention reduces the elution time of phosphate ions to 20 minutes or less under an isocratic condition that uses a low concentration hydroxide type eluent of 20 mM or less, can adequately separate fluoride ions, which are difficult to retain, from the water dip and can adequately separate chloride ions and nitrite ions, thus can shorten the measuring time in analysis that uses the above-mentioned eluent and lengthen the life of the continuous regeneration type ion exchange membrane suppressor.

Therefore, this invention is useful in a wide field of things like environment, food, agriculture, cosmetics, coating materials, semiconductor, pharmaceuticals and electric power and is especially

useful for the analysis of a number of ppb nitrite ions in the presence of a number of tens of ppm of chloride ions as in tap water analysis.

[Simple Explanation of the Figures]

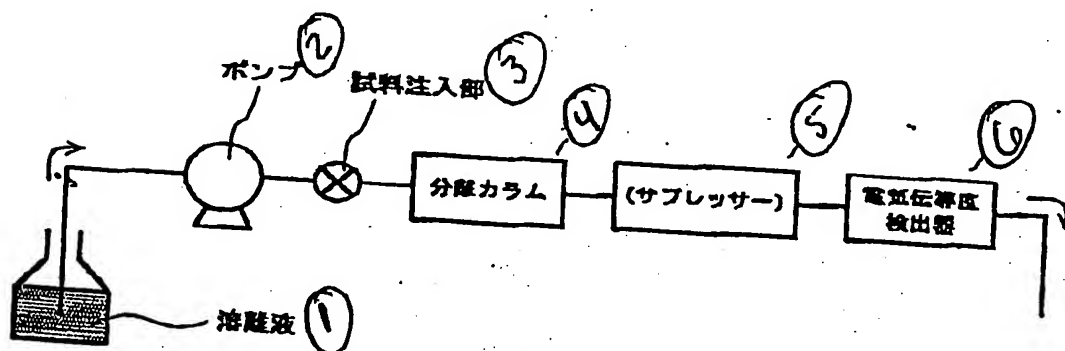
[Figure 1] is a schematic diagram showing a fundamental construction of ion chromatography.

[Figure 2] is a chromatogram that is sampled by injecting a sample aqueous solution that contains seven kinds of standard anions into a separation column prepared by packing an ion exchanger of this invention that is obtained in Example 1.

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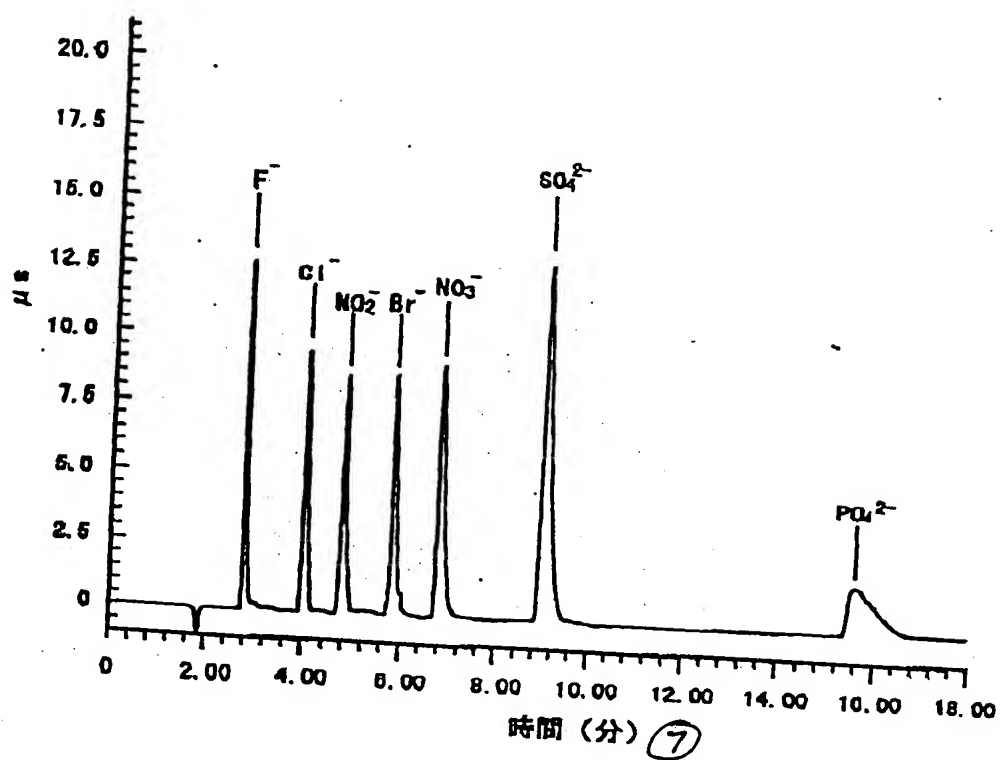
[Document Name]      Figures

[Figure 1]





[Figure 2]



Patent Filing Proof 2001-3075925

[Key to Figures 1 and 2]

- 1 Eluent
- 2 Pump
- 3 Sample Injection Area [Port]
- 4 Separation Column
- 5 Suppressor
- 6 Electrical Conductivity Detector
- 7 Time (Minutes)